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(54) Exhaust gas cleaning catalyst and process for production thereof.

(57) An exhaust gas cleaning catalyst composed of a refractory three-dimensional structure and a catalytically active substance supported thereon. That surface or part of the catalyst which makes contact with an exhaust gas is formed of numerous irregularly arranged protrusions composed of a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with refractory inorganic fibers and the catalytically active substance supported on the protrusions. The catalyst can be produced, for example, by preparing an aqueous slurry from the refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with the refractory inorganic fibers and a suitable dispersant, forming numerous irregularly arranged protrusions on that surface or part of a refractory three-dimensional structure which makes contact with an exhaust gas by using the resulting slurry, drying the structure optionally followed by calcination, depositing the catalytically active substance, and drying the calcining and resulting structure.

EP 0 211 233 A1

This invention relates to a catalyst for cleaning diesel engine exhaust gases or industrial exhaust gases containing combustible fine carbonaceous particles.

In recent years, fine carbonaceous particles in diesel engine exhaust gases (consisting mainly of solid fine carbon particles, fine particles of sulfur-containing substances such as sulfate salts, and liquid or solid high-molecular-weight fine hydrocarbon particles) have tended to give rise to an environmental hygienic problem.

5 Most of these particles have a particle diameter of less than 1 micrometer. They are liable to float in the air and be inhaled by man by respiration. Hence, rigorous restrictions on discharging of such fine carbonaceous particles from diesel engines or the like have been under

10 consideration.

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There are roughly the following two methods for removal of these fine carbonaceous particles. One is to filter an exhaust gas with a heat-resistant gas filter (for example, a ceramic foam, a wire mesh, a metal foam, or a wall-flow type ceramic honeycomb) and capture fine carbonaceous particles, and to regenerate the filter by burning the accumulated fine carbonaceous particles by a burner or the like when the pressure drop rises. The other method is to deposit a catalytic substance on a carrier having such a heat-resistant gas filter structure whereby both a filtration operation and a burning treatment are performed by using such a filter structure and the frequency of regeneration by burning is thus decreased or the burning activity of the catalyst is increased to such a degree as to require no regeneration.

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According to the former method, the rise of the pressure drop occurs early as the effect of removing the

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fine carbonaceous particles is increased. The frequency of regenerating the filter also increases. Hence, such a method is troublesome and is very disadvantageous economically. In contrast, the latter method would be much better if it employs a catalytic substance which can effectively maintain its catalytic activity under the exhaust gas discharging conditions (gas composition and temperature) in a diesel engine.

The temperature of a diesel engine exhaust gas during driving on an urban road is much lower than that from a gasoline engine, and even at an exit of a manifold, the temperature does not reach 450°C. It has been desired therefore to develop an exhaust gas cleaning catalyst which can well permit ignition and burning of accumulated fine carbonaceous particles at a temperature obtained under ordinary operating conditions of engine, for example at temperatures below 300°C. In fact, no such catalyst has ever been obtained.

It has previously been reported that with regard to catalysts for burning fine carbonaceous particles, a 7.5% rhodium/platinum alloy, a 50:50 mixture of Pt and Pd, and palladium or an alloy of palladium and not more than 75% by weight of platinum supported on tantalum oxide or cerium oxide are effective for SOF (soluble organic fraction) (GB 2,024,646).

Elsewhere, a composition comprising at least one material selected from noble metals, chromium, and catalytically active compounds thereof deposited on a porous refractory inorganic oxide and at least one bulk material selected from elements of the first transition series, silver, hafnium and catalytically active compounds thereof (US 4,303,552), and a composition comprising copper or a copper compound in combination with molybdenum or vanadium or further with platinum, rhodium, etc. (EP 92,023) have also been proposed.

With these prior art catalysts, it has been

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found difficult to fully secure the low-temperature ignitability of fine carbonaceous particles contained in diesel engine exhaust gases.

Generally, in catalysts heretofore proposed,
5 the catalytically active substances are deposited as a layer of fine catalytically active particles on that part of a three-dimensional structure which makes contact with an exhaust gas, or on wall surfaces inside internal pores of aggregate. Hence, the efficiency of contact with
10 captured fine carbonaceous particles is poor, and sufficient burning ability cannot be obtained from the catalytically active substances.

It is an object of this invention to provide a catalyst which can burn fine carbonaceous particles in an
15 exhaust gas from an automobile engine, particularly a diesel engine, at lower temperatures, and a process for producing such a catalyst.

It has now been found in accordance with this invention that in order to secure the low-temperature
20 ignitability of fine carbonaceous particles from the catalyst, the catalytically active substance should be deposited as protrusions so as to increase the efficiency of contact with the fine carbonaceous particles accumulated in layer at that surface or part of the three-dimensional structure which makes contact with an exhaust gas.

Thus, according to this invention, there is provided an exhaust gas cleaning catalyst composed of a refractory three-dimensional structure and a catalytically active substance supported thereon, wherein that surface or part of the catalyst which makes contact with an exhaust gas is formed of numerous irregularly arranged protrusions composed of a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a
35 mixture of it with refractory inorganic fibers and the catalytically active substance supported one the protrusions.

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The catalyst of this invention can be produced by a process which comprises depositing a catalytically active substance on a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture 5 of it with refractory inorganic fibers, preparing an aqueous slurry from the resulting mixture and at least one dispersant selected from the group consisting of alumina sol, titania sol, zirconia sol, silica sol, soluble boehmite and soluble organic polymer compounds, 10 forming numerous irregularly arranged protrusions on that surface or part of a refractory three-dimensional structure which makes contact with an exhaust gas by using the resulting aqueous slurry, and drying and calcining the resulting structure.

Alternatively, the catalyst of this invention 15 is produced by a process which comprises preparing an aqueous slurry from a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with refractory inorganic fibers and at least one 20 dispersant selected from the group consisting of alumina sol, titania sol, zirconia sol, silica sol, soluble boehmite and soluble organic polymer compounds, forming numerous irregularly arranged protrusions on that surface or part of a refractory three-dimensional structure which 25 makes contact with an exhaust gas by using the resulting aqueous slurry, drying the structure, optionally followed by calcination, depositing a catalytically active substance on the structure, and drying and calcining the resulting mixture.

Although the invention is in no way restricted 30 by theory, the principle of the present invention can be explained as follows:-

Fine carbonaceous particles are accumulated in layer on that part of the three-dimensional structure 35 which makes contact with an exhaust gas. Let us assume

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- that the three-dimensional structure is a wall-flow honeycomb monolithic body (a ceramic monolithic wall-flow honeycomb composed of a number of gas flow channels in which the flow channels are composed of channels having
- 5 an open inlet portion and a closed outlet portion and channels having a closed inlet portion and an open outlet portion alternately and adjacently arranged and the flow channel walls adjacent to each other are composed of a porous partition wall having a gas filter function).
- 10 When a gas passes through the pores the partition walls, fine carbonaceous particles form a bridge on the side wall surfaces at the inlet portion of pores and are accumulated there in layer in spite of the fact that the average diameter of the pores is much larger than that of
- 15 the fine carbonaceous particles. If the platinum-group element-containing catalyst is deposited in layer on the surface of the partition wall or on the aggregate inside pores of the partition wall without forming protrusions, the efficiency of contact of the catalytically active
- 20 substance with the accumulated carbonaceous particles is poor, and no desirable catalytic action is observed. In contrast, according to this invention, the contact efficiency is increased and the efficiency of burning the carbonaceous particles is very much increased since the
- 25 catalytically active substance is deposited as protrusions on the gas contacting surface or part of the three-dimensional structure.

The three-dimensional structure used in this invention may conveniently be a ceramic foam, an open-flow ceramic honeycomb, a wall flow honeycomb monolithic body, a metal honeycomb, a metal foam, etc.

The catalytically active substance used in this invention is at least one substance selected from the group consisting of platinum, rhodium, palladium, vanadium, iron, cobalt, nickel, molybdenum, tungsten, niobium, phosphorus, lead, zinc, tin, copper, chromium,

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manganese, cerium, lanthanum and silver. Of these, platinum, rhodium and palladium are especially preferred. It is also possible to use a combination of at least one catalytically active substance selected from the group consisting of platinum, rhodium and palladium and at least one substance selected from the group consisting of vanadium, iron, cobalt, nickel, monobdenum, tungsten, niobium, phosphorus, lead, zinc, tin, copper, chromium, manganese, cerium, lanthanum, silver, barium, magnesium, calcium, strontium, potassium, sodium, cesium and rubidium.

Suitable refractory inorganic powders for use in this invention include, for example, active alumina, silica, titania, zirconia, silica-alumina, alumina-zirconia, alumina-titania, silica-titania, silica-zirconia, titania-zirconia and zeolite. They must have a particle diameter in the range of 5 to 300 micrometers.

Examples of suitable refractory inorganic fibers used in this invention are glass, alumina, silica, silicon nitride (Si_3N_4), silicon carbide (SiC), potassium titanate, rock wool, zirconia, titanium carbide, iron, nickel, tungsten and calcium phosphate in the form of fibers or whiskers.

The diameter and length of the inorganic fibrous substance have strong correlation to the average particle diameter of the refractory inorganic powder used. Its diameter is preferably 1/300 to 1/5 times its average particle diameter. Inorganic fibrous substances having diameters outside this range are undesirable because fibers having too small a diameter will simply get entangled with the particles, and those having too large a diameter make it difficult to deposit the catalytically active substance as protrusions.

The length of the fibers is also correlated to the average particle diameter, and is preferably 1/10 to 20 times the average particle diameter. Those having too

small a length just fill in the interstices of the particles, and those having too large a length have poor dispersibility with the particles and will form masses consisting solely of the fibers.

5 The refractory inorganic powder, as stated above, should have a particle diameter of 5 to 300 micrometers. If the particle diameter is less than 5 micrometers, the resulting protrusions are small, and there is hardly any effect of increasing the efficiency of contact
10 with the fine carbonaceous particles. On the other hand, if the particle diameter is larger than 300 micrometers, it is difficult to form protrusions, and the area of contact of the resulting protrusions decreases. Hence,
15 the ability of the catalytically active substance to burn the fine carbonaceous particles cannot be increased too much.

The amount of the refractory inorganic fibers used, as the ratio by weight to the amount of the refractory inorganic powder, is from 1:1 to 1:0.05, particularly from 1:0.7 to 1:0.07. If the refractory inorganic fibers is used in a larger ratio, the formation of protrusions by the particles is hampered. On the other hand, if it is used in a smaller ratio, no effect of adding the refractory inorganic fibers is observed.

25 The production of the catalyst of this invention is not particularly restricted, and for example, the following processes may be cited as preferred ones.

Active alumina pellets are impregnated with an aqueous solution of a water-soluble salt of a catalytically active substance, dried and calcined. Thereafter, the calcined product is pulverized by a hammer mill (for example, PULVERIZER produced by Hosokawa Micron Co., Ltd.) and classified by a classifier (for example, MICRON SEPARATOR Model MS-O produced by Hosokawa Micron Co.,
30 Ltd.) to give a powder composed of the refractory inorganic powder having a particle size distribution
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between 5 micrometers and 300 micrometers and the catalytically active substance deposited thereon. Thereafter, the resulting powder, either alone or in combination with the refractory inorganic fibers, is put into an aqueous solution containing 1 to 20% by weight, as alumina (Al_2O_3), of soluble boehmite (for example DISPURAL made by Condea Co., Ltd.), and the mixture is stirred. By the thickening effect of the boehmite dispersant, the powdery active substance does not settle even on stopping the stirring, and a stable slurry can be obtained. The slurry is impregnated into a three-dimensional structure, and the excess of the slurry is removed. As a result, catalyst layers in the form of protrusions having a large height can be formed on the surfaces of the inner walls of the structure or on the surface of the structure. The impregnated three-dimensional structure is then dried, and calcined at 200 to 800°C, particularly 300 to 700°C.

The dispersant used may also be sols such as alumina, titania, zirconia and silica sols, and soluble organic polymer compounds besides soluble boehmite. Examples of the soluble organic polymer compounds are poly(sodium acrylate), poly(ammonium acrylate), a sodium or ammonium salt of acrylic acid/maleic acid copolymer, polyethylene oxide, polyvinyl alcohol, carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, starch, gum arabic, guar gum and glue. To make the catalyst coat layer more porous, it is possible to add a soluble organic polymer compound such as polyethylene glycol to the slurry, and remove it by calcination.

Another preferred process for producing the catalyst of this invention comprises first depositing the refractory inorganic powder (and optionally the refractory inorganic fibers) on the three-dimensional structure, further depositing a catalytically active substance on the three-dimensional structure, and drying

and calcining the resulting structure.

In the catalyst of this invention, the total amount of substances deposited including the catalytically active substance is not particularly restricted. It 5 is 10 to 200 g, preferably 20 to 150 g, per liter of the three-dimensional structure.

The amount of the refractory inorganic powder is in the range of 5 to 150 g, preferably 10 to 120 g, per liter of the three-dimensional structure. The amount 10 of the inorganic fibrous substance optionally used, as the weight ratio to the refractory inorganic powder, is advantageously from 1:1 to 1:0.05, preferably from 1:0.7 to 1:0.07.

The amount of a catalytically active substance 15 deposited is 0.01 to 70 g, preferably 0.05 to 50 g, as an oxide or metal, per liter of the three-dimensional structure.

The burning reaction of the fine carbonaceous particle is a solid-solid reaction and the efficiency of 20 contact between the catalytically active substance and the fine carbonaceous particles is a very important factor.

The present invention is characterized by the fact that the efficiency of burning is markedly increased 25 by depositing the catalytically active substance to protrusions of a suitable size composed of the refractory inorganic powder (and optionally the refractory inorganic fibers).

When refractory inorganic fibrous material is 30 used, bridging of the fine carbonaceous particles is prevented, and the efficiency of contact with the catalytically active substance is further increased. Consequently, the fine carbonaceous particles can be burnt at lower temperatures than in the absence of the inorganic 35 fibrous substance.

The following Examples and Comparative Examples

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illustrate the present invention more specifically.

EXAMPLE 1

One kilograms of commercial active alumina pellets (diameter 3 to 5 mm, surface area 150 m²/g) 5 were impregnated with 1 liter of an aqueous solution of 290 g of ammonium metavanadate and 435 g of oxalic acid, withdrawn, dried at 150°C for 3 hours, and calcined in air at 500°C for 2 hours. The pellets were pulverized by a hammer mill, and classified by a classifying device 10 so that the proportion of particles having a particle size of 5 micrometers to 30 micrometers became not more than 20%. Coarse particles having a particle diameter of more than 300 micrometers were removed by using a sieve. The resulting granular active substance had an average 15 particle diameter of 75 micrometers and contained 12.5% of particles with a size of 5 to 30 micrometers, 13.5% of particles with 30 to 45 micrometers, 22% of particles with a size of 45 to 74 micrometers, 27% of particles with a size of 74 to 105 micrometers, 12% of particles with a 20 size of 105 to 149 micrometers and 13% of particles with a size of 149 to 300 micrometers.

In an aqueous solution of 15 g (11.25 g calculated as Al₂O₃) of soluble boehmite was dispersed 150g of the classified powdery catalyst obtained above to form 25 520 ml of a stable slurry. The slurry had a viscosity of 25 cps at room temperature.

A commercial wall-flow type honeycomb monolithic body (material: cordierite; 5.66 inches in diameter, 6.0 inches in length, 100 cells/inch², wall thickness 30 17 mils) was used as a carrier. The partition walls of the carrier had an average pore diameter of 30 micrometers.

The above slurry (520 ml) was poured into the carrier from the side surface of its gas inlet portions, 35 and the excess of the slurry was removed from the opposite side by means of an air blower. The carrier was

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dried at 150°C for 3 hours, and calcined in air at 500°C for 2 hours to obtain a finished catalyst. The amounts of Al₂O₃ and V₂O₅ deposited in the finished catalyst were 40 g/liter-carrier, and 9 g/liter-carrier,
5 respectively. The catalytic substance was deposited as layers of coarse particles on the wall surface of the carrier without closing the pores of the carrier.

EXAMPLE 2

One kilogram of commercial titania pellets
10 (diameter 3 to 5 mm, surface area 30 m²/g) was immersed with 450 ml of an aqueous solution of 276 g of ammonium molybdate, dried at 150°C for 3 hours, and calcined in air at 500°C for 2 hours.

The pellets were pulverized and classified
15 (average particle diameter 65 micrometers) as in Example 1. A catalyst was prepared in the same way as in Example 1 using 150 g of the resulting classified powdery catalytically active substance. The slurry used had a viscosity of 28 cps.

20 The finished catalyst contained 40 g/liter-carrier of TiO₂ and 9 g/liter-carrier of MoO₃ deposited thereon.

EXAMPLE 3

A classified powdery catalyst was obtained by
25 depositing copper oxide (CuO) using copper nitrate [Cu(NO₃)₂.6H₂O] on titania-silica pellets (TiO₂/SiO₂ mole ratio=4/1) prepared in advance.

The powdery catalyst was deposited on a three-dimensional structure as in Example 1 to form a
30 finished catalyst which contained 40 g/liter-carrier of TiO₂-SiO₂ and 9 g/liter-carrier of CuO deposited thereon.

EXAMPLE 4

As in Example 1, each of the catalytically
35 active substances shown in Table 1 was deposited on pellets of a heat-resistant inorganic substance and a

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classified powdery catalyst was obtained. The powdery catalyst was deposited on the same three-dimensional structure in the same way as in Example 1 to give a finished catalyst.

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Table 1

Catalyst designation	Composition (g/l-carrier)	Refractory inorganic substance (g/l-carrier)
4-1	PbO ₂ (9)	Al ₂ O ₃ (40)
4-2	WO ₃ (9)	Al ₂ O ₃ (40)
4-3	CoO(9)	Al ₂ O ₃ (40)
4-4	MnO ₂ (5)-CuO(4)	ZrO ₂ (40)
4-5	Ag ₂ O(9)	SiO ₂ -Al ₂ O ₃ (4/1,40)*
A-6	CuO(4)-Cr ₂ O ₃ (4)-K ₂ O(1)	Al ₂ O ₃ (40)
4-7	Nb ₂ O ₅ (8)-BaO(1)	Al ₂ O ₃ -ZrO ₂ (3/1,40)*
4-8	NiO(7)-CeO ₂ (2)	Al ₂ O ₃ (40)

Note

* shows the composition ratio (mole ratio) of the heat-resistant inorganic substance. In the preparation of the catalysts shown in Table 1, ammonium paramanganate was used as a source of WO₃; niobium chloride, as a source of Nb₂O₅, and nitrates, as sources of the other catalytically active substances.

EXAMPLE 5

One hundred and fifty grams of MoO₃-deposited titania pulverized and classified as in Example 2 was dispersed in an aqueous solution of poly(ammonium acrylate) (AQUALIC-NL, a tradename for a product of Nippon Shokubai Kagaku Kogyo Co., Ltd.) in a concentration of 1% by weight as solids to give 520 ml of a

stable slurry. A catalyst was prepared as in Example 1 using the slurry. The finished catalyst contained 40 g/liter-carrier of TiO_2 and 9 g/liter-carrier of MoO_3 deposited thereon.

5 COMPARATIVE EXAMPLE 1

V_2O_5 -deposited alumina pellets prepared in the same way as in Example 1 were pulverized by a hammer mill and then wet-pulverized by an ordinary wet mill to give a slurry having an average particle diameter of 0.8 micrometer.

10 The slurry was impregnated in the same three-dimensional structure as used in Example 1. The excess of the slurry was removed by an air blower, and the impregnated three-dimensional structure was dried at 150°C for 3 hours, and calcined at 500°C for 2 hours to form a catalyst.

15 The amounts of Al_2O_3 and V_2O_5 deposited on the finished catalyst were 40 g/liter-carrier and 9 g/liter-carrier, respectively. The amounts of deposits in the pores, however, were larger than those on the wall surface of the carrier, and the deposition was nonuniform.

20 COMPARATIVE EXAMPLE 2

25 ZrO_2 pellets having the same composition as obtained in Example 4-4 were pulverized and then wet-pulverized by a wet mill in the same way as in Comparative Example 1 to obtain a slurry having an average particle diameter of 1.0 micrometer. A catalyst was prepared in the same way as in Example 1 using the resulting slurry. The finished catalyst contained 5 g/liter-carrier of MnO_2 , 4 g/liter-carrier of CuO and 40 g/liter-carrier of ZrO_2 deposited thereon.

30 EXAMPLE 6

35 One kilogram of the same alumina pellets as used in Example 1 were immersed in 750 ml of a nitric acid solution of dinitrodiammineplatinum containing 20g of Pt, dried at 150°C for 3 hours, and calcined at 500°C

for 2 hours. The calcined pellets were pulverized and classified to obtain a Pt-deposited powder having a particle size distribution between 5 micrometers and 300 micrometers. The average particle diameter of the powder was 81 micrometers. The product was deposited on the same three-dimensional structure as in Example 1 to prepare a catalyst containing 50 g/liter-carrier of Al_2O_3 and 1.0 g/liter-carrier of Pt deposited thereon.

EXAMPLE 7

10 Two kilograms of the same alumina pellets as in Example 1 were immersed in 1.4 liters of a mixture of a nitric acid solution of dinitrodiammineplatinum containing 15 g of Pt and an aqueous solution of rhodium nitrate containing 1.67 g of Rh, dried at 150°C for 3 hours, 15 and calcined at 500°C for 2 hours.

The calcined pellets were pulverized and classified in the same way as in Example 1 to give a powdery catalyst having an average particle diameter of 78 micrometers and containing Pt and Rh deposited thereon. One 20 kilogram of the classified powdery catalyst was dispersed in an aqueous solution of 100 g (75 g as alumina) of soluble boehmite to form 2 liters of stable slurry.

The slurry had a viscosity of 72 cps at room temperature. A commercial open honeycomb monolithic body 25 (material: cordierite; 5.66 inches in diameter, 6.0 inches in length, 300 cells/inch², wall thickness 6 mils) was used as a carrier.

The carrier was immersed in the slurry and withdrawn, and the excess of the slurry was removed by an 30 air blower. The carrier was then dried at 150°C for 3 hours, and calcined in air at 500°C for 2 hours.

The finished catalyst contained 120 g/liter-carrier of Al_2O_3 , 0.9 g/liter-carrier of Pt and 0.1 g/liter-carrier of Rh.

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EXAMPLE 8

One kilogram of the same alumina pellets as in

Example 1 were impregnated with 750 ml of an aqueous solution of 630.7 g of cerium nitrate [Ce(NO₃)₃.6H₂O], dried at 150°C for 3 hours, and calcined at 500°C for 2 hours. The calcined product was then impregnated with 5 750 ml of a nitric acid solution of dinitrodiammine-platinum containing 25 g of Pt, dried at 150°C for 3 hours and calcined at 500°C for 2 hours. The calcined product was pulverized and classified in the same way as in Example 1 to give a powdery catalyst having an average 10 particle diameter of 79 micrometers.

The resulting powdery catalyst (150 g) was dispersed in an aqueous solution of 15 g, as SiO₂ of silica sol (Snowtex-O, a tradename for a product of Nissan Chemical Co., Ltd.) to give 520 ml of a stable 15 slurry. A catalyst was prepared using the slurry and the same carrier as used in Example 1.

The finished catalyst contained 40 g/liter-carrier of Al₂O₃, 10 g/liter-carrier of CeO₂ and 1.0 g/liter-carrier of Pt deposited thereon.

20 EXAMPLE 9

Example 7 was repeated except that a commercial ceramic foam (bulk density 0.35 g/cm³; porosity 87.5%, volume 1.7 liters) was used as a carrier instead of the open honeycomb monolithic body.

25 The resulting finished catalyst contained 120 g/liter-carrier of Al₂O₃, 0.9 g/liter-carrier of Pt and 0.1 g/liter-carrier of Rh deposited thereon.

EXAMPLE 10

Catalysts having the compositions indicated in 30 Table 2 below were prepared by the same methods as in Examples 6 to 9. Ammonium paramolybdate was used as a source of molybdenum; ammonium dihydrogen phosphate, as a source of phosphorus; ammonium paragungstate, as a source of tungsten; niobium pentachloride, as a source of 35 niobium; and nitrates, as sources of other catalytically active substances.

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Table 2

Catalyst designation	Carrier	Refractory inorganic powder (g/l-carrier)	Platinum-group element (g/l-carrier)	Base metal element (g/l-carrier)
10-1	Wall-flow monolithic body	Alumina(40)	Pt(1)	Fe ₂ O ₃ (8)
10-2	"	"	"	CoO ("")
10-3	"	"	"	NiO ("")
10-4	"	"	"	MoO ₃ ("")
10-5	"	"	"	WO ₃ ("")
10-6	"	"	"	Nb ₂ O ₅ ("")
10-7	"	"	"	P ₂ O ₅ ("")
10-8	"	"	"	PbO ("")
10-9	"	"	"	ZnO ("")
10-10	"	"	"	SnO ₂ ("")
10-11	"	"	"	CuO ("")
10-12	"	"	"	Mn ₃ O ₄ ("")
10-13	"	"	"	CeO ₂ ("")
10-14	"	"	"	La ₂ O ₃ ("")
10-15	"	"	"	AgO ("")
10-16	"	"	"	BaO ("")
10-17	"	"	"	MgO ("")
10-18	"	"	"	K ₂ O (2)
10-19	Ceramic foam	TiO ₂ -SiO ₂ * (4/1,100)	Pt(1)	SnO ₂ (8)
10-20	"	TiO ₂ -ZrO ₂ * (4/1,100)	"	" (8)
10-21	"	Zeolite	"	" (8)
10-22	Wall-flow monolithic body	Alumina(40)	Pd(2)-Rh(0.2)	None

Note: * shows the mole ratio of oxides.

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COMPARATIVE EXAMPLE 3

Pt-deposited alumina pellets prepared as in Example 6 were pulverized, thereafter wet-pulverized by a wet mill to such an extent as to perform ordinary wash 5 coating. As a result, 520 ml of a slurry with an average particle diameter of 1.1 micrometers was obtained. A catalyst was prepared by the same method as in Example 1 except that the resulting slurry was used. The resulting finished catalyst contained 50 g/liter-carrier of Al_2O_3 10 and 1.0 g/liter-carrier of Pt deposited on it.

COMPARATIVE EXAMPLE 4

Pt/Rh-deposited alumina pellets prepared as in Example 7 were pulverized, and then wet-pulverized by a wet mill to such an extent as to perform ordinary wash 15 coating. As a result, a slurry having an average particle diameter of 1.0 micrometer was prepared. An open honeycomb monolithic supported catalyst was prepared by using the resulting slurry. The finished catalyst contained 120 g/liter-carrier of Al_2O_3 , 0.9 g/litrer-carrier of Pt 20 and 0.1 g/liter-carrier of Rh deposited thereon.

COMPARATIVE EXAMPLE 5

An Al_2O_3 -deposited open honeycome monolithic catalyst was prepared in the same way as in Example 7 except that Pt and Rh were not used.

25 COMPARATIVE EXAMPLE 6

A catalyst was prepared in the same way as in example 8 except that 1316 g of chromium nitrate $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ was used instead of 630.7 g of cerium nitrate. The finished catalyst contained 40 g/liter- 30 carrier of Al_2O_3 , 10 g/liter-carrier of Cr_2O_3 and 1.0 g/liter-carrier of Pt deposited thereon.

EXAMPLE 11

Alumina powder having deposited thereon platinum was prepared as in Example 6. The powder had an average 35 particle diamter of 81 micrometers. The resulting powdery

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catalyst (150 g) was dispersed in an aqueous solution containing 15 g (11.25 g as Al_2O_3) of boehmite to give 520 ml of a stable slurry. Ten grams of commercial alumina fibers (average diameter 9 micrometers, average length 900 micrometers) were dispersed in the slurry with stirring. The viscosity of the slurry was 25 cps at room temperature. A catalyst was prepared as in Example 1 using the resulting slurry and the same three-dimensional structure as used in Example 1.

The finished catalyst contained 50 g/liter-carrier of Al_2O_3 , 1.0 g/liter-carrier of Pt and 3.3 g/liter-carrier of alumina fibers deposited thereon.

EXAMPLE 12

Two kilograms of the same alumina pellets as in Example 1 were immersed in 1.4 liters of a mixture of a nitric acid solution of 15 g, as Pt, of dinitrogdiammine-platinum and an aqueous solution of 1.67 g, as Rh, of rhodium nitrate, dried at 150°C for 3 hours, and calcined at 500°C for 2 hours.

The calcined product was pulverized and classified in the same way as in Example 1 to give a powdery catalyst having an average particle diameter of 78 micrometers and containing Pt and Rh deposited thereon. One kilogram of the classified powdery catalyst was dispersed in an aqueous solution of 100 g (75 g as Al_2O_3) of soluble boehmite to give 2 liters of a stable slurry.

One hundred grams of commercial silicon carbide whiskers (average diameter 0.7 micrometer, average length 80 micrometers) were dispersed in the slurry with stirring.

The viscosity of the slurry was 91 cps (room temperature). The same open honeycomb monolithic carrier as used in Example 7 was immersed in the slurry, and withdrawn. The excess of the slurry was removed by an air blower. The impregnated carrier was then dried at 150°C for 3 hours, and calcined in air at 500°C for 2

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hours to give a finished catalyst.

The finished catalyst contained 120 g/liter-carrier of Al_2O_3 , 0.9 g/liter-carrier of Pt, 0.1 g/liter-carrier of Rh and 12 g/liter-carrier of silicon carbide whiskers deposited thereon.

5 EXAMPLE 13

One kilogram of commercial silica-alumina pellets (alumina content 13%, diameter 3 to 5 mm, surface area $230 \text{ m}^2/\text{g}$) was impregnated in 750 ml of an aqueous solution of 371 g of lead nitrate [$\text{Pb}(\text{NO}_3)_2$], dried at 150°C for 3 hours, and then calcined at 500°C for 2 hours. The calcined product was pulverized and classified in the same way as in Example 1 to give a powdery catalyst having an average particle diameter of 82 micrometers.

10 The classified powdery catalyst (150 g) was dispersed in an aqueous solution of 15 g, as SiO_2 , of silica sol (Snowtex-O, a tradename for a product of Nissan Chemical Co., Ltd.), and then 10 g of commercial glass fibers (average diameter 13 micrometers, average length 200

15 micrometers) were put into the dispersion. With stirring, the mixture was dispersed to give 520 ml of a stable slurry. A catalyst was prepared as in Example 1 using the resulting slurry and the same three-dimensional structure as in Example 1.

20 The finished catalyst contained 40 g/liter-carrier of silica-alumina, 10 g/liter-carrier of PbO, 1.0 g/liter-carrier of Pt and 3.3 g/liter-carrier of glass fibers deposited thereon.

25 EXAMPLE 14

30 A catalyst was prepared in the same way as in Example 12 except that a commercial ceramic foam (bulk density 0.35 g/cm^3 , porosity 87.5 %, volume 1.7 liters) was used as a carrier instead of the open honeycomb monolithic carrier. The finished catalyst contained 120

35 g/liter-carrier of Al_2O_3 , 0.9 g/liter-carrier of Pt, 0.1 g/liter-carrier of Rh and 12 g/liter-carrier of

silicon carbide whiskers.

EXAMPLE 15

Catalysts having the compositions indicated in
Table 3 were prepared by the same methods as in Examples
5 11 to 14.

Ammonium paramolybdate was used as a source of
molybdenum; ammonium dihydrogen phosphate, as a source of
phosphorus; ammonium paratungstate, as a source of
tungsten; niobium pentachloride, as a source of niobium;
10 and nitrates, as sources of other catalytically active
substances.

Table 3

Catalyst design-nation	Carrier	Refractory inorganic powder (g/ ℓ -carrier)	Inorganic fibers (g/ ℓ -carrier)	Platinum-group element (g/ ℓ -carrier)	Base metal element (g/ ℓ -carrier)
15-1	Wall-flow monolithic body	Alumina (40) 87 μm *1	Alumina fibers (3.3) 6 (δ) - 300 (ℓ) μm *2	Pt (1)	Fe ₂ O ₃ (10)
15-2	"	"	Si ₃ N ₄ whiskers (3.3) 0.5 (δ) - 40 (ℓ) μm	"	" (10)
15-3	"	"	Silica fibers (3.3) 10 (δ) - 1000 (ℓ) μm	"	" (10)
15-4	"	"	Silicon carbide whiskers (3.3) 0.6 (δ) - 80 (ℓ) μm	"	CoO (10)
15-5	"	"	"	"	NiO (10)
15-6	"	"	"	"	MoO ₃ (10)
15-7	"	"	"	"	WO ₃ (10)
15-8	"	"	"	"	Nb ₂ O ₅ (10)
15-9	"	"	"	"	P ₂ O ₅ (10)
15-10	"	"	"	"	PbO (10)
15-11	"	"	"	"	ZnO (10)
15-12	"	"	"	"	SnO ₂ (10)

- to be continued -

Table 3 (continued)

Catalyst design- nation	Carrier	Refractory inorganic powder (g/ ℓ - carrier)	Inorganic fibers (g/ ℓ - carrier)	Platinum- group element (g/ ℓ - carrier)	Base metal element (g/ ℓ - carrier)
15-13	Wall-flow monolithic body	Alumina(40) 87 μm *1	Silicon carbide whiskers (3.3) 0.6(δ)-80(ℓ) μm	"	CuO (10)
15-14	"	"	"	"	Mn ₃ O ₄ (10)
15-15	"	"	"	"	CeO ₂ (10)
15-16	"	"	"	"	La ₂ O ₃ (10)
15-17	"	"	"	"	AgO (5)
15-18	"	"	"	"	BaO (5)
15-19	"	"	"	"	MgO (5)
15-20	"	"	"	"	K ₂ O (5)
15-21	Ceramic foam	TiO ₂ -SiO ₂ (4/1,100)	Silicon carbide whiskers (10) 0.6(δ)-80(ℓ) μm	Pt(0.9) Rh(0.1)	CeO ₂ (10)
15-22	"	TiO ₂ -ZrO ₂ (4/1,100)	"	Pt(1)	" (10)
15-23	"	Zeolite(100)	"	"	" (10)
15-24	"	Mullite (100)	"	"	" (10)
15-25	Wall-flow monolithic body	Alumina (40)	Silicon carbide whiskers (3.3) 0.6(δ)-80(ℓ) μm	Pd(2)- Rh(0.2)	None

*1: Average particle diameter
 *2: diameter (δ) and length (ℓ)
 *3: Mole ratio of oxides

EXAMPLE 16

The same alumina pellets as used in Example 1 were pulverized and classified to give an alumina powder having an average particle diameter of 90 micrometers and 5 a particle size distribution between 5 micrometers and 300 micrometers.

The classified alumina powder (150 g) was dispersed in an aqueous solution containing 15 g, as SiO_2 , of silica sol (Snowtex-O, a tradename for a 10 product of Nissan Chemical Co., Ltd.), and then 10 g of commercial glass fibers (average diameter 13 micrometers, average length 2200 micrometers) were put into the dispersion. The mixture was dispersed with stirring to give 520 ml of a stable slurry. The same open honeycomb 15 monolithic carrier was immersed in the slurry, and withdrawn. The excess of the slurry was removed by an air blower. The impregnated carrier was then dried at 150°C for 3 hours, and calcined in air at 500°C for 2 hours to give a carrier having the alumina powder and glass 20 fibers deposited thereon as protrusions.

The carrier was then immersed in 4 liters of an aqueous solution containing a nitric acid solution of 2.47 g, as Pt, of dinitrodiammineplatinum to deposit platinum by chemisorption, dried at 150°C for 3 hours, 25 and calcined at 600°C for 2 hours.

The finished catalyst contained 50 g/liter-carrier of Al_2O_3 , 3.3 g/liter-carrier of glass fibers and 1 g/liter-carrier of Pt deposited thereon.

COMPARATIVE EXAMPLE 7

30 Pt-deposited alumina pellets prepared as in Example 6 were pulverized and then wet-pulverized by a wet mill to such an extent as to perform ordinary wash coating. As a result, 520 ml of a slurry having an average particle diameter of 0.9 micrometer was obtained. 35 Ten grams of alumina fibers were put into the slurry and dispersed with stirring. Otherwise, the same operation

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as in Example 11 was carried out to give a finished catalyst containing 50 g/liter-carrier of Al_2O_3 , 1.0 g/liter-carrier of Pt and 3.3 g/liter-carrier of alumina fibers deposited thereon.

5

COMPARATIVE EXAMPLE 8

Example 12 was repeated except that the silicon carbide whiskers were not used. The resulting finished catalyst contained 120 g/liter-carrier of Al_2O_3 , 0.9 g/liter-carrier of Pt and 0.1 g/liter-carrier of Rh deposited thereon.

10

COMPARATIVE EXAMPLE 9

Example 12 was repeated except that Pt and Rh were not used. The resulting finished catalyst contained 120 g/liter-carrier of Al_2O_3 and 12 g/liter-carrier of silicon carbide whiskers deposited thereon.

15

COMPARATIVE EXAMPLE 10

Example 13 was repeated except that 1316 g of chromium nitrate $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ was used instead of 371g of lead nitrate. The resulting finished catalyst contained 40 g/liter-carrier of silica-alumina, 10 g/liter-carrier of Cr_2O_3 , 1.0 g/liter-carrier of Pt, and 3.3 g/litrer-carrier of glass fibers.

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EXAMPLE 17

The catalysts obtained in Examples 1 to 16 and Comparative Examples 1 to 10 were evaluated by using a 4-cylinder diesel engine with a displacement of 2300 cc. At an engine rotating speed of 2500 rpm and a torque of 4.0 kg-m, fine particles were captured for about 2 hours. Thereafter, the torque was increased every 5 minutes by an increment of 0.5 kg-m, and variations in the pressure drop of the catalyst layer were continuously recorded. The temperature (T_e) at which the rise of the pressure due to accumulation of the fine particles became equal to the fall of the pressure due to combustion of the fine particles and the temperature (T_i) at which the fine particles were ignited and burnt and the pressure drop

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fell abruptly. The amount of the pressure drop changed per hour in the case of capturing fine particles at an engine rotating speed of 2500 rpm and a torque of 4.0 kg-m was calculated from the chart, and the value 5 ΔP (mmHg/hr) was determined. Furthermore, the amounts of fine particles at the inlet and outlet of the catalyst layer were measured, and the percent removal (ratio of capturing) of the fine particles was calculated. The results are shown in Tables 4 to 6.

Table 4

Catalyst designation	ΔP (mmHg/Hr)	Te (°C)	Ti (°C)	Ratio of capturing (%)
Example 1	22	323	338	70
" 2	20	325	342	70
" 3	20	343	360	70
" 4-1	21	340	362	70
" 4-2	24	374	390	70
" 4-3	22	352	366	70
" 4-4	20	343	350	70
" 4-5	24	345	360	70
" 4-6	21	338	352	70
" 4-7	23	372	388	70
" 4-8	21	347	362	70
" 5	21	325	343	70
Comp. Ex. 1	27	365	380	70
" 2	25	388	412	70

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Table 5

Catalyst designation	ΔP (mmHg/Hr)	T _e (°C)	T _i (°C)	Ratio of capturing (%)
Example 6	7	310	320	70
" 7	3	308	319	40
" 8	6	309	320	70
" 9	5	275	288	30
" 10-1	7	308	318	70
" 10-2	6	307	318	70
" 10-3	6	307	318	70
" 10-4	7	308	320	70
" 10-5	6	305	316	70
" 10-6	6	305	316	70
" 10-7	5	300	314	70
" 10-8	7	308	320	70
" 10-9	7	310	320	70
" 10-10	6	305	316	70
" 10-11	7	310	317	70
" 10-12	7	308	319	70
" 10-13	5	305	315	70
" 10-14	6	310	320	70
" 10-15	6	308	318	70
" 10-16	7	309	320	70
" 10-17	7	308	319	70
" 10-18	6	308	318	70
" 10-19	5	272	285	30
" 10-20	5	273	287	30
" 10-21	6	275	288	30
" 10-22	7	315	330	70
Comp. Ex. 3	7	395	403	70
" 4	4	392	400	5
" 5	18	565	575	5
" 6	11	385	400	70

Table 6

Catalyst designation	ΔP (mmHg/Hr)	Te (°C)	Ti (°C)	Ratio of capturing (%)
Example 11	8	303	315	73
" 12	4	300	311	45
" 13	8	301	312	75
" 14	6	270	282	33
" 15-1	8	300	312	74
" 15-2	7	298	310	72
" 15-3	7	300	312	74
" 15-4	7	299	310	73
" 15-5	7	299	310	73
" 15-6	8	300	312	74
" 15-7	7	297	309	72
" 15-8	7	298	310	74
" 15-9	6	295	308	72
" 15-10	8	300	312	74
" 15-11	8	301	314	74
" 15-12	7	295	308	73
" 15-13	8	301	313	74
" 15-14	8	300	312	74
" 15-15	7	296	308	73
" 15-16	7	301	313	73
" 15-17	7	300	312	72
" 15-18	8	300	313	73
" 15-19	8	298	310	74
" 15-20	7	300	312	73
" 15-21	6	266	280	35
" 15-22	6	268	282	34
" 15-23	6	270	282	33
" 15-24	6	272	285	33
" 15-25	7	311	324	73
" 16	4	302	313	42
Comp. Ex. 7	7	390	405	70
" 8	3	309	320	5
" 9	18	565	580	40
" 10	13	382	398	72

What is claimed is:

1. An exhaust gas cleaning catalyst composed of a refractory three-dimensional structure and a catalytically active substance supported thereon, wherein that surface or part of the catalyst which makes contact with an exhaust gas is formed of numerous irregularly arranged protrusions composed of a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with refractory inorganic fibers and the catalytically active substance supported on the protrusions.
2. The catalyst of claim 1 wherein the refractory three-dimensional structure is a ceramic foam, an open-flow ceramic honeycomb, a wall-flow honeycomb monolithic body, a metal honeycomb or a metal foam.
3. The catalyst of claim 1 wherein the refractory three-dimensional structure is a ceramic monolithic wall-flow honeycomb composed of a number of gas flow channels in which the flow channels are composed of channels having an open inlet portion and a closed outlet portion and channels having a closed inlet portion and an open outlet portion alternately and adjacently arranged and the flow channel walls adjacent to each other are composed of a porous partition wall having a gas filter function.
4. The catalyst of claim 1 wherein the refractory inorganic powder is a powder of at least one material selected from the group consisting of active alumina, silica, titania, zirconia, silica-alumina, alumina-zirconia, alumina-titania, silica-titania, silica-zirconia, titania-zirconia and zeolite.
5. The catalyst of claim 1 wherein the refractory inorganic fibers are at least one kind of fibers selected from the group consisting of fibers and whiskers of glass, alumina, silica, silicon nitride (Si_3N_4), silicon carbide (SiC), potassium titanate, rock wool,

zirconia, titanium carbide, iron, nickel, tungsten and calcium phosphate.

6. The catalyst of claim 1 wherein the average diameter and average length of the refractory inorganic fibers are from 1/300 to 1/5, and from 1/10 to 20 times the average particle diameter of refractory inorganic powder, respectively.

7. The catalyst of claim 1 wherein the weight ratio of the refractory inorganic powder and the refractory inorganic fibers is in the range of from 1:0.05 to 1:1.

8. The catalyst of claim 1 wherein the catalytically active substance is at least one substance selected from the group consisting of platinum, rhodium, palladium, vanadium, iron, cobalt, nickel, molybdenum, tungsten, niobium, phosphorus, lead, zinc, tin, copper, chromium, manganese, cerium, lanthanum and silver.

9. The catalyst of claim 8 wherein the catalytically active substance is platinum, rhodium, or palladium.

10. The catalyst of claim 1 wherein the catalytically active substance is a mixture of at least one element selected from the group consisting of platinum, rhodium and palladium and at least one element selected from the group consisting of vanadium, iron, cobalt, nickel, molybdenum, tungsten, niobium, phosphorus, lead, zinc, tin, copper, chromium, manganese, cerium, lanthanum, silver, barium, magnesium, calcium, strontium, potassium, sodium, cesium and rubidium.

11. A process for producing an exhaust gas cleaning catalyst comprising a refractory three-dimensional structure and a catalytically active substance supported thereon, which comprises depositing the catalytically active substance on a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with refractory inorganic fibers, preparing an

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aqueous slurry from the resulting structure and at least one dispersant selected from the group consisting of alumina sol, titania sol, zirconia sol, silica sol, soluble boehmite and soluble organic polymer compounds, forming numerous irregularly arranged protrusions on that surface or part of the refractory three-dimensional structure which makes contact with an exhaust gas by using the resulting slurry, and drying and calcining the resulting structure.

12. A process for producing an exhaust gas cleaning catalyst comprising a refractory three-dimensional structure and a catalytically active substance supported thereon, which comprises preparing an aqueous slurry from a refractory inorganic powder having a particle diameter of 5 to 300 micrometers or a mixture of it with refractory inorganic fibers and at least one dispersant selected from the group consisting of alumina sol, titania sol, zirconia sol, silica sol, soluble boehmite and soluble organic polymeric compounds, forming numerous irregularly arranged protrusions on that surface or part of the refractory three-dimensional structure which makes contact with an exhaust gas by using the resulting slurry, drying the structure, optionally calcining it, depositing the catalytically active substance on the structure, and drying and calcining the resulting structure.

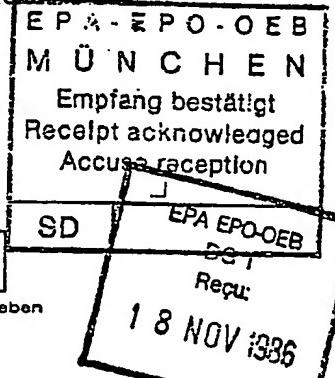
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November 11, 1986

Re: European patent application 86 108 950.6
Nippon Shokubai Kagaku Kogyo Co., Ltd.

Referring to Rule 88 EPC, we are submitting new pages 2, 4, 5, 6, 12, 17, 19, 24, 25 and 31 (in triplicate) in which we have carried out the following amendments:

- Page 2, line 11: "mini-" was amended to "mani-";
page 4, line 22: "bohemite" was amended to "boehmite";
page 5, line 10: "the pores the partition" was amended to "the pores in the partition";
page 6, line 7: "monobdenum" was amended to "molybdenum";
page 12, Table 1: "A-6" was amended to "4-6";
page 17, line 35: "diamter" was amended to "diameter";
page 19, line 18: "commerciial" was amended to "commercial";
page 24, lines 28, 33, 34 and 35: "fine particles" was amended to "fine carbonaceous particles";
page 25, lines 2, 6 and 8: "fine particles" was amended to "fine carbonaceous particles"; and
page 31, line 7 from the bottom: "polymeric" was amended to "polymer".

We submit that these amendments are corrections of obvious typographical errors in the sense of Rule 88 EPC and should be allowable.



European Patent Attorney

Encls.:

New pages 2, 4, 6, 12,
17, 19, 24, 25 and 31
(each in triplicate)



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EUROPEAN SEARCH REPORT

0211233

Application number

EP 86 10 8950

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
Y	US-A-4 404 007 (TOSHIYUKI TUKAO) * Claim 1; column 3, lines 29-48; figure 4 *	1,3,4, 8,10- 12	B 01 D 53/36 B 01 J 37/02
Y	GB-A-2 091 584 (W.R. GRACE & CO.) * Claims 1-5,13-15; page 1, lines 24-32,48-53; page 2, lines 38-44; page 3, lines 10-38 *	1,3,4, 8,10- 12	
A	DE-A-2 304 351 (KALI-CHEMIE AG) * Claims 1,3,6,8-12 *	1,2,5, 8,10, 12	
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 D 53/00 B 01 J 37/00 B 01 D 46/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 31-10-1986	Examiner POLESAK, H.F.	
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